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IX. *On the Composition of certain Essential Oils.* By ROBERT KANE, M.D., M.R.I.A., *Professor of Natural Philosophy to the Royal Dublin Society and of Chemistry to the Apothecaries' Hall of Ireland, Corresponding Member of the Society of Pharmacy and of the Society of Medical Chemistry of Paris, Honorary Member of the Society of Apothecaries of the North of Germany, &c.*

Read 12th June, 1837.

THE analyses, which constitute the material of this paper, were undertaken as the first step in a train of research, which had for its object the solution of two problems in organic chemistry, the importance of which will be at once recognized; namely, first, whether there exists a law connecting the composition of the oils derived from the same natural family of plants? and secondly, what is the chemical nature of the essential oils as a class? is the oil of bitter almonds a type for all? Towards a decision of these questions some materials have been collected; but the investigation embraces a field so wide, that considerable time must elapse, before even such general results, as have been already obtained, can be worked into a form fit for publication. In the meantime I am induced to lay before chemists those conclusions with respect to the composition of some of the oils, which may serve as data in a solution of the first question, and as initiatory to the more abstract considerations on their composition as a class.

I. COMPOSITION OF OIL OF ROSEMARY.

The oil of rosemary, obtained in its purest commercial form, is colourless, and possesses strongly the odour of the fresh plant. Its specific gravity is given by Brande 0.9118. I found the oil of commerce to be 0.897; but like all these oils it differs according to seasons, from the variable quantity of stearopten it may hold dissolved. When submitted to rectification it distils over, the boiling point rising, but not rapidly; and the last portion in the retort becomes brown,

and of a thick consistence. By repeated distillations it can be rendered completely pure.

Its specific gravity is then from 0.8854 to 0.8875. Berzelius states the specific gravity of the pure oil to be 0.889. It boils at a temperature from 332° to 334° Fahr. Its boiling point is almost absolutely constant,—indeed much more constant than that of any other oil I have examined. It was analyzed in the ordinary way by combustion with oxide of copper, and the carbonic acid collected, by potash, in Liebig's apparatus.

A. Material = 0.300 gramme, gave

Water = 0.315

Carbonic acid = 0.907

B. Material = 0.247 gramme gave

Water = 0.261

Carbonic acid = 0.744

Hence follows

	A.	B.
Carbon	= 83.49	83.31
Hydrogen	= 11.66	11.66
Oxygen	= 4.85	5.03

These analyses, having been made with quantities of oil distilled at different times, and coinciding so completely, rendered it unnecessary to increase the number.

The above result is fully expressed by the formula $c_{45} H_{38} O_2$, which gives

c_{45}	= 276.3	83.63
H_{38}	= 38.0	11.54
O_2	= 16.0	4.83
	<hr/>	<hr/>
	330.3	100.00

Evidently $c_{45} H_{38} O_2 = 9(C_5 H_4) + 2HO$; that is, we may consider oil of rosemary as a hydrate of one of those numerous oils, agreeing in per-cent composition with oil of turpentine. This relation induced me to make some experiments on the action of various bodies on it, the results of which belong properly to a future memoir, but of which I shall transcribe one here.

When mixed with sulphuric acid, oil of rosemary becomes black, and neutralized

by lime gives a soluble salt, which contains an acid belonging to the class composed of oxygen, sulphur, and an organic element. If the mixture of oil of rosemary and sulphuric acid be distilled, there is obtained a fluid possessing an aromatic, yet alliaceous odour, resembling that of mesitylene. When quite pure this fluid has a specific gravity 0.8678, and boils at about 344° Fahrenheit. It gives, on analysis, the same composition as oil of turpentine; but I shall defer the details to the memoir on the Chemical Habitues of the Oils as a Class. To this fluid I have given the name of *Rosmarine*; but I have not determined its atomic weight, so as to be able to say whether oil of rosemary be a bi-hydrate of rosemarine, and its formula $C_{45}H_{36} + 2HO$. I use the word bi-hydrate here, merely in order to represent the abstraction of $2HO$ by the sulphuric acid, and not wishing to involve any consideration of theory, which will be discussed in its proper place in the memoir already alluded to.

II. OIL OF MARJORAM.—(ORIGANUM VULGARE)

This oil is found in commerce nearly pure. Its specific gravity is variable; Mr. Brande found it 0.909; while I obtained 0.8901. This arises from the quantity of stearopten which it contains not being constant, though generally large. By rectification several times, so as to deprive it of the solid matter, it is obtained finally of the specific gravity 0.8673, the boiling point being almost completely constant at 322° F. In this state it was analyzed.

A. Material = 0.368 gramme gave

Water = 0.368

Carbonic acid = 1.154

B. Material = 0.2907 gramme gave

Water = 0.300

Carbonic acid = 0.905

C. Material = 0.2854 gramme gave

Water = 0.295

Carbonic acid = 0.891

D. Material = 0.2881 gramme gave

Water = 0.302

Carbonic acid = 0.898

Hence there is per cent.

	A.	B.	C.	D.
Carbon	= 86.71	86.08	86.33	86.18
Hydrogen	= 11.11	11.44	11.44	11.64
Oxygen	= 2.18	2.48	2.23	2.18

These results are expressible by a very simple formula, $C_{50} H_{40} O$, or $10 \{C_5 H_4\} + O$, which gives

C_{50}	= 307	86.48
H_{40}	= 40	11.27
O	= 8	2.25

The first analysis deviates a little from this result, in the direction opposite to that generally taken by errors of experiment in organic analysis, but so trivially, that I am not inclined to attribute to it any importance. From the remarkable relation of the formula to that of oil of turpentine, it may, perhaps, be thought that possibly the oil of origanum had the same composition, and that the two per cent. attributed to oxygen, arose from the loss consequent on an imperfect combustion; but that idea is disproved by—first, the uniformity of the analyses which were made at different times and on different quantities of oil; and secondly, by the fact that in only the fourth analysis does the hydrogen amount to what oil of turpentine should yield, that is 11.55 per cent., the general error in analysis being to give too high a value for the hydrogen. The stearopten of this oil would appear to contain much more oxygen than the oil itself; as a quantity of oil which contained some, and had consequently a boiling point of 344° , gave the following results:

Material	= 0.360 gramme gave
Water	= 0.350
Carbonic acid	= 1.100

Hence per cent.

Carbon	= 84.48	} 100
Hydrogen	= 10.80	
Oxygen	= 4.72	

being a mixture, it admits of no formula.

III. OIL OF PEPPERMINT.

This oil had been submitted to analysis by Blanchet and Sell,* but their results having been communicated without any detail, and the analyses being exceedingly discordant, I was obliged to reexamine its constitution before I could satisfy my mind. The result has been, that I have obtained a formula differing from that of the chemists before named.

The oil of peppermint of commerce, particularly that sold as American, is often adulterated by a large quantity of oil of turpentine, from which, if once mixed, no number of rectifications can completely purify it. The rough oil, when pure, has, according to Brande, a specific gravity 0.907; I found it 0.9083. It contains a certain quantity of stearopten, though not so much as the generality of oils; when freed from this by repeated distillations it has a specific gravity of 0.8998, and boils between 370° and 380° Fahr.

The following are the analytical results :

A. Material = 0.2905 gramme gave

Water = 0.318

Carbonic acid = 0.812

B. Material = 0.3667 gramme gave

Water = 0.407

Carbonic acid = 1.035

C. Material = 0.3443 gramme gave

Water = 0.375

Carbonic acid = 0.969

Hence there is per cent.

	A.	B.	C.
Carbon	= 77.29	78.06	77.81
Hydrogen	= 12.11	12.32	12.01
Oxygen	= 10.60	9.62	10.18

The analyses A and B were made with the same specimen of oil; the correct value for carbon is therefore that of B. The analysis C was made subsequently with a different specimen.

* Journal de Pharmacie, vol. xx. 1834.

The formula $C_{21}H_{20}O_2$ gives

C_{21}	=	128.9	78.14	} 100
H_{20}	=	20.0	12.12	
O_2	=	16.0	9.74	

I cannot explain the difference between this result and that of Blanchet and Sell, as they give no account of the circumstances under which their analyses were made. They make no mention of having submitted their oil to rectification. Their result is $C_{12}H_{10}O$, and per cent.

	Experiments.		Theory.	} 100
Carbon	= 79.63	79.53	80.35	
Hydrogen	= 11.25	10.77	10.90	
Oxygen	= 9.12	9.70	8.75	

Blanchet's result for the stearopten of oil of peppermint, though discordant with itself, yet approaches closer to mine for the oil. Thus he obtained for the solid crystalline stearopten $C_{10}H_{10}O$, and per cent.

	Experiments.		Mean.	Theory.	} 100
Carbon	= 79.63	77.27	78.45	77.28	
Hydrogen	= 11.25	12.96	12.11	12.59	
Oxygen	= 9.12	9.77	9.44	10.12	

On analyzing the first portion obtained in rectifying oil of peppermint, which had a boiling point about ten degrees lower than the general mass subsequently condensed, I obtained the following result :

Material = 0.337 gramme gave

Water = 0.360

Carbonic acid = 0.969

Hence per cent.

Carbon = 79.53

Hydrogen = 11.86

Oxygen = 8.61

This result might be considered as approximating to that of Blanchet; but this portion could not be considered as being pure oil, as it constituted not a tenth of the quantity submitted to distillation. I attributed its different composition to an adulteration by oil of turpentine, which from its greater volatility came over in the commencement. If the oil of turpentine were in large quantity, a complete rectification could not be obtained.

Upon the whole it is evident, that we cannot consider the nature of the oil and stearopten of peppermint as being absolutely determined; at the same time, I conceive myself justified in placing some confidence in my results, from their agreement, and the care with which the substance had been purified.

IV. OIL OF PENNYROYAL.—(MENTHA PULEGHIUM)

The oil of pennyroyal is stated by Mr. Brande to have a specific gravity of 0.939. I could not obtain it in commerce with a specific gravity higher than 0.9271. I consider, however, the specimens having that specific gravity as being pure, and that a higher density arises from dissolved stearopten. The oil of 0.9271 having been rectified, left but little solid matter; and the pure oil, after distillation, had a specific gravity of 0.9255. Its boiling point could not be obtained quite constant, fluctuating between 360° and 370° Fahr. At the end of this paper a few remarks on the boiling points of these oils will be found. It was analyzed as follows:

A. Material = 0.3607 gramme gave		
Water	=	0.353
Carbonic acid	=	1.020
B. Material = 0.3014 gramme gave		
Water	=	0.297
Carbonic acid	=	0.861

Hence per cent.

	A.	B.	
Carbon	= 78.2	79.0	} 100.0
Hydrogen	= 10.8	10.9	
Oxygen	= 11.0	10.1	

These analyses give the formula $C_{10}H_8O$, or

Carbon	= 61.4	79.30
Hydrogen	= 8.0	10.35
Oxygen	= 8.0	10.35
	<hr/>	<hr/>
	77.4	100.00

This result is exceedingly remarkable, as from it follows that oil of penny-

royal has the same composition as camphor, and as the new substance described by me in the memoir on Acetone, and which I have termed *Dumasine*.* A very interesting problem, which I hope soon to be able to solve, will be, to determine the relative changes which dumasine and oil of pennyroyal undergo, in the circumstances under which common camphor yields camphoric acid.

Oil of pennyroyal is more frequently adulterated with oil of turpentine, and to a greater extent, than any other oil that I know of. I have found specimens, which delivered four-fifths of their volume of pure oil of turpentine on rectification. Thus, in the commencement of these experiments, I isolated and analyzed quantities of the product of rectification of commercial oil of pennyroyal, and stated verbally at a meeting of the Academy, that I could not find any difference between rectified oil of pennyroyal and oil of turpentine. I shall detail a couple of the analyses, made under those circumstances, because the result may be used as a test for the closeness of the other experimental results, and for the legitimacy of the formulæ deduced from them.

Fluid obtained by rectifying impure oil of pennyroyal, specific gravity = 0.8673; boils constant at 315°.

A. Material = 0.2183 gramme gave
 Water = 0.232
 Carbonic acid = 0.697

B. Material = 0.2433 gramme gave
 Water = 0.260
 Carbonic acid = 0.779

Hence

	A.	B.	Theory.
Carbon	= 88.29	88.56	88.45
Hydrogen	= 11.78	11.87	11.55

Its formula C_5H_4 . It was oil of turpentine.

* It had been my intention to insert the account of the composition and properties of *Dumasine* as an appendix to the memoir on Pyroacetic Spirit, but it has been withheld in order, when further studied, to form the subject of an independent paper. A notice of its discovery and composition was published in the Proceedings of the Royal Irish Academy, No. IV. page 61, and copied from thence into the Philosophical Magazine for 1837.

V. OIL OF SPEARMINT.—(MENTHA VIRIDIS.)

The oil of spearmint is stated by Brande to have a specific gravity 0.939. That which I found in commerce had, in the rough state, a specific gravity 0.9142, and when freed by distillation of a considerable quantity of stearopten, 0.876. It boiled pretty constantly at 320° F. It gave by analysis as follows :

A. Material = 0.3087 gramme gave	
Water	= 0.311
Carbonic acid	= 0.954
B. Material = 0.350 gramme gave	
Water	= 0.350
Carbonic acid	= 1.075
C. Material = 0.4284 gramme gave	
Water	= 0.439
Carbonic acid	= 1.327

Hence the per cent. composition :

	A.	B.	C.	
Carbon	= 85.44	84.94	85.66	} 100.0
Hydrogen	= 11.19	11.11	11.38	
Oxygen	= 3.36	3.95	2.96	

These results give the formula $c_{35}H_{28}O$; that is,

c_{35}	= 214.9	85.67	} 100.0
H_{28}	= 28.0	11.15	
O	= 8.0	3.18	
	<hr/> 250.9	<hr/> 100.0	

This formula, like that of oil of origanum, may be represented by a multiple of oil of turpentine + oxygen = $7 \{c_5H_4\} + O$. It is however impossible to make any deduction from these facts with respect to its nature.

VI. OIL OF LAVENDER.—(LAVANDULA SPICA.)

The oil of lavender is remarkable for containing, probably, more stearopten than any other essential oil, the quantity itself being variable with the season and

with the climate. Thus, in the oil from the south of Europe (Murcia), it is said to amount to more than one-half its weight, and I have often found a fourth of the English oil to remain behind on distillation, so loaded with stearopten as to become quite solid on cooling. These circumstances,—the quantity of solid matter, and its not differing very much in volatility from the oil,—present great obstacles to the obtaining oil of lavender in an absolutely pure condition.

The oil examined by Mr. Brande, and which probably contained much stearopten, was found by him of a specific gravity 0.9206. In the specimen which I tried the specific gravity was 0.9174. By repeated rectifications, by which as much of the solid matter as possible was separated, it was obtained 0.8865, and then boiled at 370° F. Another portion equally rectified had a specific gravity 0.8745, and boiled at 365° F. Saussure, who likewise examined this oil, states its specific gravity, when pure, to be 0.877.

A specimen of the commercial oil, the specific gravity of which was 0.9172, was rectified, and the product received in four different vessels, stopping when the residue in the retort appeared to become thick.

No. 1	had sp. gr. = 0.8864	} All boiled between 360° and 370°.
2	= 0.8879	
3	= 0.8884	
4	= 0.9050	

boiled at 390°.

The residue solidified by cooling. The difficulty of pronouncing on the absolute purity of any one portion of oil of lavender is thus evident.

The analysis of this oil was conducted in the usual way. Different portions of oil were selected, in consequence of their boiling points and specific gravities not being in accordance.

A. Specimen sp. gr. = 0.8865 ; boiling point = 370° F.

Material = 0.4333 gramme gave

Water = 0.441

Carbonic acid = 1.245

B. Specimen sp. gr. = 0.8745 ; boiling point 365°.

Material = 0.2835 gramme gave

Water = 0.299

Carbonic acid = 0.819

C. Specimen sp. gr. = 0.8864; boils at from 365° to 370°.

Material = 0.3788 gramme gave

Water = 0.394

Carbonic acid = 1.079

Hence the composition

	A.	B.	C.
Carbon	= 79.45	75.77	78.81
Hydrogen	= 11.30	11.73	11.55
Oxygen	= 9.25	12.50	9.64

As it is quite evident that, the heavier this oil is, the more stearopten it contains, and consequently, the less pure it is; and as, by Dumas's analysis, stearopten, if not completely identical, has at least the same composition with common camphor, I am inclined to consider the high values for carbon in the oils used in analyses A and C as owing in great part to its presence, and to assign the analysis B as a closer approximation to the composition of the pure oil. With this idea agrees Saussure's old result, who from an oil of the sp. gr. 0.877 obtained the composition

Carbon	= 75.50	} 100.0
Hydrogen	= 11.07	
Oxygen	= 13.07	
Nitrogen	= 0.36	

The nitrogen being now acknowledged to result from imperfections in the method employed, the tendency of which was also generally to give an underestimate for the amount of hydrogen, his result is found to agree with that of analysis B; but whether from both oils being pure, or from both being equally impure, I cannot undertake to say.

Under such circumstances it is scarcely useful to attempt the construction of a formula, as representing the result obtained. $C_{15}H_{14}O_2 = 3C_5H_4 + 2HO$, may, however, be employed:

Thus,	C_{15}	=	92.1	75.5
	H_{14}	=	14.0	11.5
	O_2	=	16.0	13.0
			<hr/>	<hr/>
			122.1	100.0
				x 2

I must not be understood as stating positively this formula to represent the truth.

ADDITIONAL REMARKS.

There is a peculiarity in the method of ebullition of these oils which renders it very difficult to fix upon a certain fixed temperature as the boiling point, but rather compels us to consider the oil as boiling within a limit of temperature, sometimes extending to ten degrees of Fahrenheit. Thus, in taking the boiling point of an oil in a tube, a thermometer being immersed therein to some distance above the bulb, the oil will enter into full ebullition apparently at 355°, and the temperature of the thermometer, on continuing the boiling for five or ten minutes, will gradually rise to 360° or 365°, and will not then stop so completely, but that an ebullition continued for five or six minutes more, may produce a further rise of a couple of degrees. If the oil be allowed to cool, and be then again heated, the same phenomenon will be repeated, and so, as often as may be wished; but the most colourless oil, when thus frequently heated, gradually becomes brown, and then there is a permanent elevation of the boiling point, arising from decomposition.

I attribute this phenomenon to an unequal distribution of heat through the mass, and to the heat being supplied by the spirit lamp too rapidly to be carried off from the oil by the vapour formed at the limited surface of contact of the oil with the air in the tube. This is supported by the fact, that by moderating the heat the boiling point may be kept constant; but, by a suitable heat, it may be kept constant at any degree, between the limits already alluded to. This is the reason why the boiling points of the oils analyzed are generally given within a limit of a few degrees. Some cases where the boiling points were almost really constant, I attribute to a closer approach to absolute purity in the oil.

A great deficiency exists in analytical results obtained under circumstances such as those described in the present paper, from the total want of a control over their exactitude; and one or two words on the nature of these controlling results, with reference to obtaining such in our experiments, may be here of use. There are four modes of control—1st, by synthesis, which is the most complete, but which in organic chemistry is attainable only in some very few

cases. Of these few, the synthesis of urea, and that of acetic acid, may be taken as illustrations. 2nd, The method next in completeness is the breaking up of the body into other compounds whose composition is already known; as, formal into formic acid and methylic alcohol; acetal into acetic acid and vinic alcohol; acetic acid into carbonic acid and acetone. 3rd, The determination of the atomic weight of the body, by the compounds into which it enters with other well known substances. Thus the composition of oxalic ether controls the analysis of sulphuric ether, and the salts of the vegetable alcaloids give the only means of verifying the composition of the base itself. The fourth method of control is limited to such bodies as pass into vapour without being decomposed, and then the density of the vapour should stand in some simple relation to the sum of the densities of the constituents, taken in the atomic proportions given by analysis. Thus the discussion as to whether naphthaline was represented by the formula $C_{10}H_8$ or $C_{10}H_6$ was decided by the vapour possessing a density immediately following from the former, but inconsistent with the latter. That, however, we must not insist on very simple relations, is shown by the complex numbers found for some of the inorganic compounds by Mitscherlich and Dumas.

Now in examining the composition of the oils, we are debarred from efficiently exerting any of these methods of control:—1st, we cannot generate them by synthesis; 2nd, we do not as yet know their chemical nature sufficiently to break them up into other bodies with which we can get more definite results; and 3rd, their combinations with other bodies have not been as yet developed. Towards the application of these methods I have made some progress in the cases of oils of rosemary, lavender, and oil of turpentine, which all give with sulphuric acid and a base, soluble salts, of which that from turpentine alone has been completely analyzed. The atomic weight of turpentine from the salt of lime is found to be $C_{20}H_{16}$; the same as from artificial camphor; and the salt has the composition $SO_3 \cdot CaO \cdot + C_{20}H_{16}$, belonging to a series distinct from the sulpho-vinates on the one hand, and the sulpho-naphthalates upon the other, and being probably an analogue to the sulpho-mesitylic acid described in my memoir upon Acetone. I mention these results, although they properly belong to a different paper, in order to point out the probable means of applying the methods of control to the essential oils in future investigations. I attempted very often to determine the densities of the vapours of the essential oils with a bath of

chloride of zinc, but I never obtained a result on which I could with satisfaction rely. The residual oil was evidently altered in its nature and appearance, and there always remained in the globe a certain quantity of permanent gas. I attribute the imperfect success of these attempts, to the mutual action of the oil and air of the globe at the high temperature necessary for the experiment; but by a modification of the apparatus I may possibly at a future period succeed.

A circumstance connected with the purification of the oils employed in the analyses detailed in this paper requires some notice here, as it has not been adverted to under the special heads; namely, the means used to secure the perfect freedom of the oils from water. This is the more important, as particularly in the results obtained with the oils of marjoram and spearmint, the small quantity of oxygen might be conceived as being derivable from this source, unless proper precaution had been taken. The oils, previous to rectification, were in all cases digested for several days on recently fused chloride of calcium; then poured off, and distilled; and the portions selected for analysis allowed to remain in contact for about twelve hours with a few pure fragments of chloride of calcium, before being used. In no case did the oil appear to act on, or dissolve any of the fused salt; and hence it was only necessary to pour the oil off from the chloride, and not to again distil it, in order to obtain it pure.